Synthesis, Characterization, Swelling Studies and Dye Removal of Chemically Crosslinked Acrylic Acid/Acrylamide/N,N-Dimethyl Acrylamide Hydrogels

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Abstract: Polymeric hydrogels of acrylic acid (AA), acrylamide (AAm) and N,N-Dimethylacrylamide (DMAm) were prepared by free-radical polymerization at 70°C in methanol, using allylpentaerythritol (APE) as a multifunctional crosslinker and benzoyl peroxide (BPO) as an initiator. The effects of DMAm concentration and variation of pH solutions on the swelling behavior of polymers were investigated. Also AA/AAm/DMAm hydrogel was used in experiments on adsorption of a water soluble monovalent cationic dye such as Basic Blue 9 (BB-9; Methylene blue). FT-IR results confirmed the Structural features of the obtained hydrogels. Results from SEM observation showed a three dimensional porous structure of the hydrogels. Thermogravimetric analysis (TGA) of hydrogels was performed to investigate the thermal properties. The swelling results showed an increase of the swelling of AA/AAm/DMAm hydrogels as the content of DMAm increases in the hydrogel. The swelling percentage and swelling kinetics parameters such as initial swelling rate and swelling rate constant were determined. It was also shown that the swelling of hydrogels increased with the increase of pH and the maximum extent was reached at pH 8 in all compositions. The uptake of BB-9 to AA/AAm/DMAm hydrogel is studied by batch adsorption technique at 25°C. The hydrogel in the dye solution showed coloration. Kinetics and isotherms of dye adsorption were also studied. It was found that the adsorption kinetics of hydrogels followed a pseudo-second-order model. Equilibrium isotherms were analyzed using the Langmuir and Freundlich isotherms. It was seen that the Freundlich model fits the adsorption data better than the Langmuir model.

Keywords: Hydrogel, Swelling, Dye Removal, Cationic Dye, Adsorption, Kinetics, Isotherms, N, N-Dimethylacrylamide

1. Introduction

The use of dyes in industries like textile, dying, printing, cosmetics, food coloring, papermaking, etc. can generate colored effluents. Dyes usually have a synthetic origin and complex aromatic molecular structures which are more stable and more difficult to biodegrade [1]. Discharging of dyes which are very toxic into water resources even in a small amount can cause serious ecological problems. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms and humans [2–4]. Therefore, dye pollutionin water stream is a major environmental problem.

Methylene blue is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of humans and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5].

The methods for removing dyes from industrial colored wastewaters could require many processes such as coagulation and flocculation [6], membrane separation [7], oxidation or ozonation [8, 9], electro-coagulation [10] and adsorption [11]. Among these methods, adsorption is

generally preferred due to high efficiency, easy handling and availability of different adsorbents [12].

Nowadays, there is a great interest in the development of new adsorbents having high adsorption capacity and fast adsorption rate for wastewater treatment. Among the various adsorbents, hydrogels gained much attention in recent years. Hydrogels possessing different functional groups have been investigated in the preceding literature for this purpose [13–16].

Hydrogels are composed of hydrophilic homopolymer or copolymer network and can swell in the presence of water. Chemical cross-links (covalent bonds) or physical junctions (e.g., secondary forces, crystallite formation and chain entanglements) provide the hydrogels unique swelling behavior and three-dimensional structure [17, 18]. These materials are of great interest due to their promising applications such as heavy metal adsorption [19, 20], wound dressing [21], superabsorbent [22, 23], adsorbent for dye removal [24] and drug-delivery systems [25, 26]. Many attempts have been made to develop new hydrogels through methods such as irradiation and chemically crosslinking. Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution. In recent years, considerable researches have been done on the characterization and swelling behaviour of synthetic hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent [27-32]. They can also show stimuli-responsive properties to the various external parameters such as temperature, pH, solvent composition and salt composition depending on the type of functional groups in the structure [33, 34].

The present work was aimed to synthesize polymeric hydrogels based on N,N-Dimethylacrylamide (DMAm) with acrylic acid (AA) and acrylamide (AAm) using allylpentaerythritol (APE) as crosslinking agent. The effect of DMAm monomer on the dynamic and equilibrium swelling behavior of hydrogels in distilled water and in buffers of pH 4 and 8 at 25±0.1°C was investigated. In this work, it has been aimed to study a convenient method for removing the water soluble monovalent cationic dye such as Basic Blue 9 (Methylene blue) from aqueous solutions by adsorption on novel polymeric adsorbent such as AA/AAm/DMAm hydrogels. The adsorption kinetics and isotherms for BB-9 dye onto the hydrogels were also studied.

2. Experimental

2.1. Materials

The Acrylic acid (AA), Acrylamide (AAm) and N,N-Dimethylacrylamide (DMAm) were produced by Sigma-Aldrich Company Ltd based in UK. Allylpentaerythritol (APE) and Benzoyl peroxide (BPO) were supplied by Merck. Basic Blue 9 (Methylene blue; MB) spectroscopic grades

used in sorption studies were purchased from Fluka (USA). The chemical structures of the monomers employed in polymerization as well as the structure of BB-9 are shown in Figure 1. Double distilled water was used for polymerizations, swelling and adsorption experiments.

2.2. Synthesis of Hydrogels

Hydrogels were prepared by free-radical crosslinking polymerization of AA, AAm and DMAm in methanol using BPO as initiator. APE was used as crosslinking agent. 2.5 g of acrylamide, 2.5 g of acrylic acid and 50 mg of APE were dissolved in 20 mL methanol, and then 0.2, 0.4, 0.6, 0.8, 1 g of DMAm were added to the alcoholic solution of AA/AAm (Table 1). The polymerization was initiated by the addition of 1 mL of 5% (w/v) solution of BPO in methanol. After bubbling nitrogen for 15 min, the reaction was carried out in 100 ml two-necked round-bottom flask fitted with a reflux condenser and a thermometer. The mixture was kept at 70°C for 2 h. The produced samples were washed several times with water to remove the uncrosslinked polymer and unreacted monomers from hydrogels. The extracted gels were dried in vacuum oven at 40°C to constant weight and stored in desiccators containing anhydrous calcium chloride, as a desiccant agent, for further use. The produced hydrogels were characterized by FT-IR as well as the thermal properties.
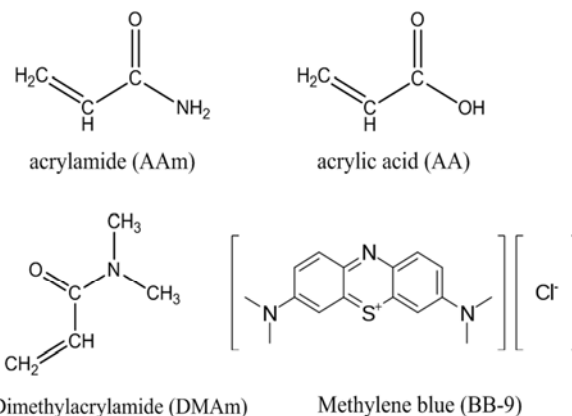

Figure 1. Chemical structures of the monomers and the Methylene blue.

Table 1. Feed composition for the prepared hydrogels.

Sample	AA/g	AAm/g	DMAm/g	APE/mg	BPO/mL	Yield %
P1	2.5	2.5	0.2	50	1	>98
P2	2.5	2.5	0.4	50	1	>98
P3	2.5	2.5	0.6	50	1	>98
P4	2.5	2.5	0.8	50	1	>98
P5	2.5	2.5	1	50	1	>98

2.3. Swelling measurements

The swelling behaviors of weighed dried hydrogel samples were carried out by immersion in distilled water at room temperature. The gels were gently wiped and weighed to determine the water absorbed at various time intervals. The

Swollen gels were weighed by an electronic balance (SARTORIUS) with an accuracy of ±0.0001 g. The effect of pH on the swelling properties was studied using buffers of pH 4 and 8. All swelling studies were carried out in 150 mL of swelling medium. The swelling studies were carried out until equilibrium in swelling was reached. Swelling measurements were done two or three times. The total uncertainly for all experiments ranged from 3 to 5%. The swelling ratio was calculated using the following equation:

$$\%S = \frac{M_t - M_o}{M_o} \times 100 \qquad (1)$$

Where, M_t and M_o refer to the weight of swollen hydrogel at time t and at time 0, respectively.

The equilibrium degree of swelling S_{eq}, after hydrogels had swollen to equilibrium in the swelling media was calculated using the following equation:

$$\%S_{eq} = \frac{M_{eq} - M_o}{M_o} \times 100 \qquad (2)$$

Here, M_{eq} is the mass of the swollen hydrogel sample at equilibrium.

The water absorbed by AA/AAm/DMAm hydrogels is quantitatively represented by the equilibrium water content (EWC) [35, 36], where

$$EWC = \frac{M_{eq} - M_o}{M_{eq}} \qquad (3)$$

2.4. Characterization Techniques

The Fourier transform infrared (FT-IR) spectra of the prepared hydrogels were recorded on a Nicolet 400D FT-IR spectrometer, using KBr pellets. Thermal properties were examined using a Simultaneous DSC-TGA (USA) Q600-SDT System from TA Instruments. The temperature range covered was 25–600°C and the scanning rate 10 °C min^{-1}, under nitrogen atmosphere. Scanning electron microscopy (SEM) analysis was carried out using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun.1n. Prior to examination, samples were gold-sputter coated to render them electrically conductive.

2.5. Adsorption Studies

2.5.1. Preparation of the Dye Solution

Methylene blue (λ_{max}: 663 nm, molecular formula: $C_{16}H_{18}N_3SCl$, nature: basic blue, and molecular weight: 319) was used as an adsorbate and was not purified prior to use. An accurately weighed quantity of the dye (0.1 g) was dissolved in double distilled water to prepare a 100 mg L^{-1} stock solution. Experimental solutions of various concentrations were prepared by further dilutions of the stock solution. The absorbance of these dilute solutions was measured on a UV–visible spectrophotometer. Standard curves were prepared by plotting the absorbance values against the concentrations.

2.5.2. Adsorption Experiments

Prior to the dye adsorption, accurately weighed hydrogels (12 mg) were immersed in water for at least 12 h to achieve the swelling equilibrium. Adsorption experiments were carried out at room temperature, in cylindrical glass vessels, by using batch conditions. In these experiments, the swollen samples of the prepared hydrogels were immersed in MB dye solutions (10 ml) with concentration of 100 mg/L. The amount of residual dye in the solution was determined at regular time using a PERKIN-ELMER UV–Vis spectrophotometer. All of the experiments were performed in triplicate and the average was used in this work. Dependence of adsorption capacities on time was determined and adsorption kinetics was investigated in detail. The influence of pH on MB removal was studied by adjusting MB solutions (100 mg/L) to different pH values (3.0, 4.0, 7.0 and 8.0) using a pH meter (DELTA-320).

The amounts of adsorbed dye per unit mass of adsorbent at time t (Q_t, $mg\ g^{-1}$) and at equilibrium (Q_e, $mg\ g^{-1}$) were calculated by using the following expressions:

$$Q_{t\ (mg/g)} = \frac{(C_i - C_t)\ V_{(L)}}{m_{(g)}} \qquad (4)$$

$$Q_{e\ (mg/g)} = \frac{(C_i - C_e)\ V_{(L)}}{m_{(g)}} \qquad (5)$$

Where C_i and C_e are the initial and equilibrium concentrations of dye (mg/L), respectively and C_t is dye concentration at time t, V is the volume of the solution added (L) and m is the amount of polymer (g).

2.5.3. Adsorption Kinetics and Isotherms
(i) Kinetic Models

The pseudo first-order and pseudo second-order kinetic models were used to predict the dye adsorption behaviors of the prepared hydrogels. The pseudo-first-order equation is generally suitable for the initial stage of the adsorption, but the pseudo-second-order equation predicts the adsorption behavior over the whole process. The kinetics of adsorption was determined by analyzing the dye adsorbed from aqueous solution at various time intervals, and then fitting the data to the two models. The pseudo first-order rate equation is given as [37, 38]:

$$\ln(Q_e - Q_t) = lnQ_{e1} - K_1 t \qquad (6)$$

Where, Q_e and Q_t are the amounts of adsorbed dyes by the hydrogel at equilibrium (mg/g) and at contact time t, respectively. Q_{e1} and k_1 show the theoretical equilibrium adsorption and pseudo first-order adsorption rate constant (min^{-1}), respectively.

The pseudo second-order kinetic model is given below: [37, 38].

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{e2}^2} + \frac{t}{Q_{e2}} \qquad (7)$$

Where Q_{e2} and k_2 are the theoretical equilibrium adsorption and pseudo second-order adsorption rate constant ($g\ mg^{-1}\ min^{-1}$), respectively.

(ii) Isotherm Models

The Langmuir and Freundlich isotherms are widely applied to describe the equilibrium adsorption isotherm data. The Langmuir isotherm is based on the hypothesis that uptake occurs on a homogeneous surface by monolayer adsorption, without interaction between the adsorbent and adsorbate [39]. The linear equation can be expressed as
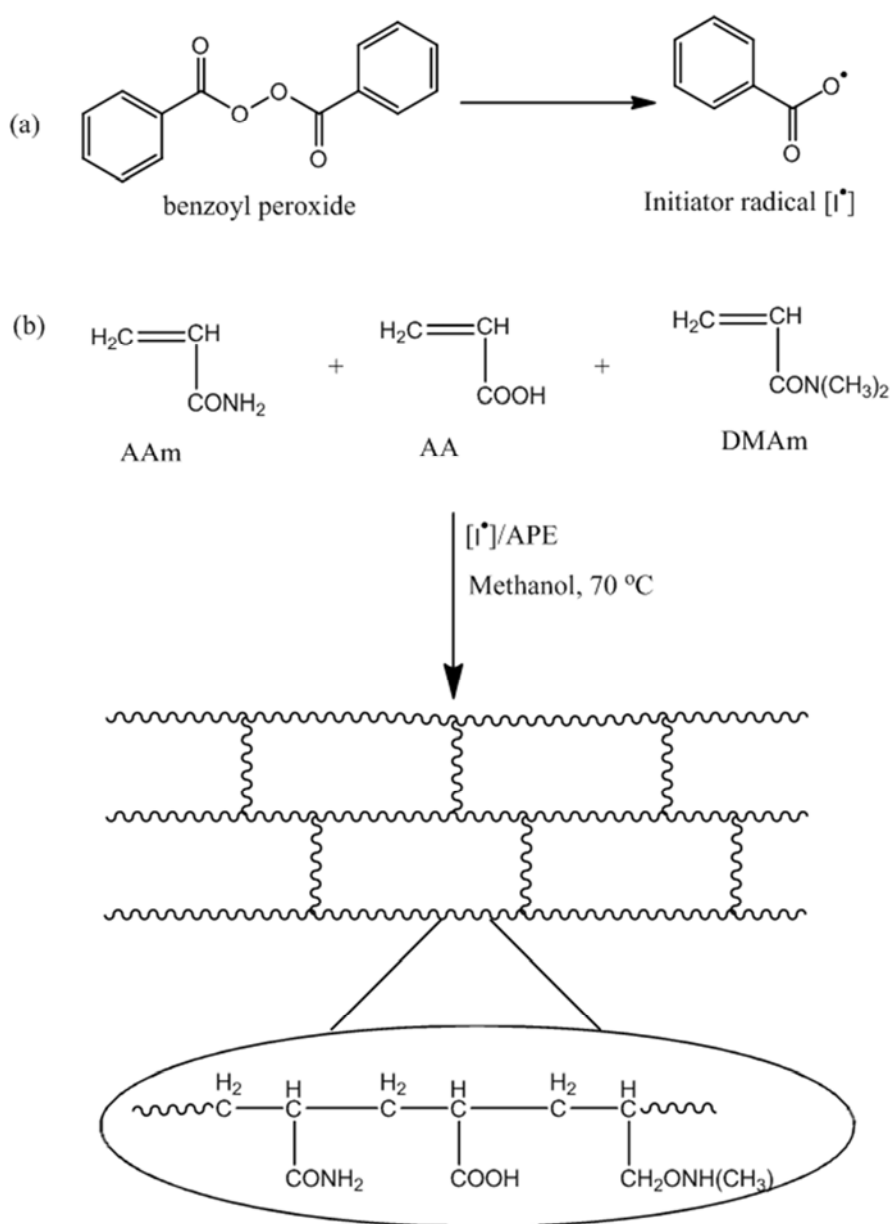
$$\frac{C_e}{Q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (8)$$

Where, C_e is the equilibrium concentration of adsorbate (*mg/L*); Q_e is the amount of dye adsorbed per gram of the adsorbent at equilibrium (*mg/g*); q_m is maximum monolayer coverage capacity (*mg/g*) and K_L is Langmuir isotherm constant (*L/mg*). In this case, the values of q_m and K_L are computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e.

The Freundlich isotherm is generally used to describe the non-ideal adsorption on heterogeneous surfaces, suggesting multilayer adsorption on adsorbent surfaces. The linear form of the Freundlich isotherm [40] is given by the following equation:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \qquad (9)$$

Where, K_f is Freundlich isotherm constant (*L/g*); n is related to adsorption intensity; C_e is the equilibrium concentration of adsorbate (*mg/L*) and Q_e is the amount of dye adsorbed per gram of the adsorbent at equilibrium (*mg/g*). The constant K_f is an approximate indicator of adsorption capacity, while *1/n* is a function of the strength of adsorption. The values of K_f and n were calculated from the intercept and slope of the plots of $\log Q_e$ against $\log C_e$.

Figure 2. *(a) Formation of initiator radicals, (b) Formation of AA/AAm/DMAm hydrogel*

3. Results and Discussion

3.1. Synthesis and FT-IR Analysis of Hydrogels

In the present investigation, the hydrogel samples were synthesized via crosslinking free radical polymerization of AA, AAm and DMAm in a methanol as polymerization medium using APE as a crosslinking agent. The procedure is described in details in the experimental section. The possible step in the polymerization reaction can be explained as follow: Upon heating the reaction mixture primary radicals begin to generate via homolytic decomposition of the BPO (Figure 2a) to produce benzoyl radicals. These radicals rapidly react with the three monomers, i.e., AA, AAm and DMAm or the APE crosslinker molecules to produce the primary radicals. These monomer radicals undergo propagation and termination reaction to form crosslink hydrogels, as shown in Figure 2b, that do not dissolve in the reaction medium. Their insolubility is due to the formation of permanent links between the polymeric chains. The presence of functional groups in the prepared hydrogel samples was evaluated via FT-IR spectra as shown in Figure 3. The broad absorption band at 3439 cm^{-1} is ascribed to the existence of –OH and –NH groups [41]. The bands at 2924 and 2855 cm^{-1} are ascribed to aliphatic C-H stretching vibration. The bands at 1652–1684 cm^{-1} can be attributed to carbonyl groups of acrylamide and carboxylic acid [15, 42]. The band around 1529 cm^{-1} is ascribed to stretching flexural vibrations of N–H group. The characteristic absorption bands around 1245 and 1031 cm^{-1} are due to the stretching vibration of N-CH$_3$. The vinyl bands at 1680 cm^{-1} did not appear in spectra indicating that all monomeric groups are involved in the polymerization reaction [27, 43].
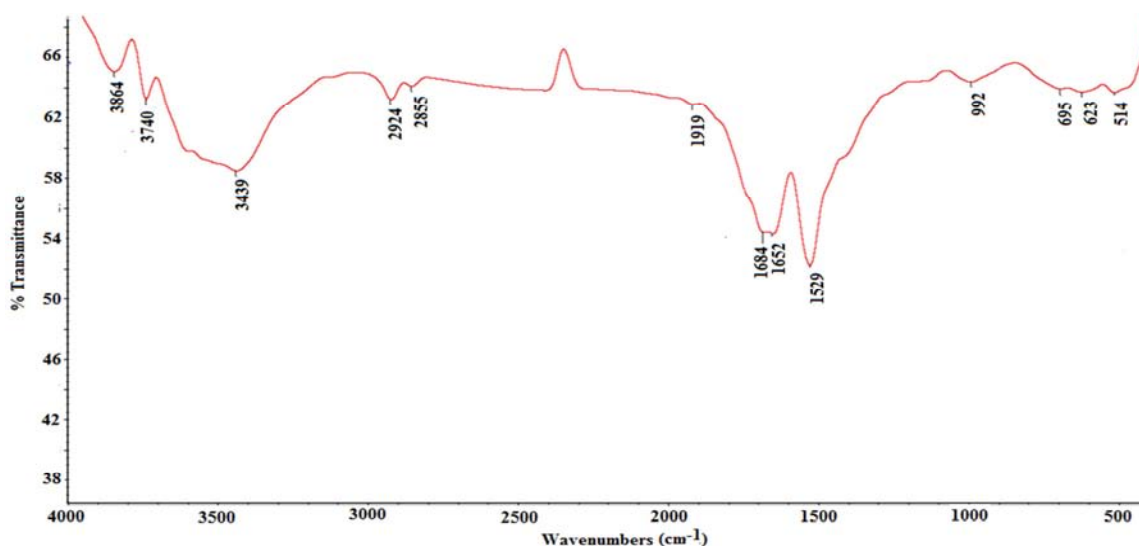

Figure 3. Representative FT-IR spectrum of AA/AAm/DMAm hydrogel

3.2. Swelling Studies

The hydrogels were placed in a known amount of distilled water, buffer pH 4 and buffer pH 8 solutions (150 mL) and allowed to swell. The initial weight of the gel was compared to the swollen weight. This allows for a transient analysis of the swelling of hydrogel. The weights of the swollen gel were measured at time intervals. The water was absorbed in the gel thus increasing the weight of the gel with time until equilibrium swelling weight is reached. While weighing the gels, care was taken to remove the solvent on the surface, so that only the weight of the water incorporated into the hydrogel was considered. The percentage swelling (%S) of the hydrogels in distilled water and in buffers of pH 4 and 8 was calculated from equation (1) (as mentioned in experimental section). The effect of hydrophilic monomer DMAm on the swelling behavior was studied by fixing concentration of AA, AAm and APE while the DMAm was changed to be 0.2, 0.4, 0.6, 0.8 and 1 g. The dynamic swelling behavior of AA/AAm/DMAm hydrogels in distilled water, buffer of pH 4 and buffer of pH 8 is shown in Figure 3(a-c). It can be seen that percentage swelling of the hydrogels increases with time until a certain level, when it becomes constant. This value of percentage swelling may be named equilibrium swelling percentage (%S_{eq}). The swelling studies were carried out until equilibrium in swelling was reached.

The results in Table 2 showed that, the values of equilibrium swelling of AA/AAm/DMAm hydrogels range from 1757-2984 % in distilled water, 1424-2607 % at pH 4 and 2769-4068 % at pH 8 at different concentrations of DMAm. As shown in Figure 4 the values of the equilibrium swelling of AA/AAm/DMAm hydrogels increase with increasing the concentration of DMAm monomer from 0.2 g to 1 g. The reason of this is the hydrophilicity of DMAm monomer. The more hydrophilic groups in the AA/AAm/DMAm hydrogels get more swelling and this also the reason that made the values of the equilibrium swelling increase from P1 sample to P5 sample. This is an expected result about swelling of AA/AAm/DMAm hydrogels.
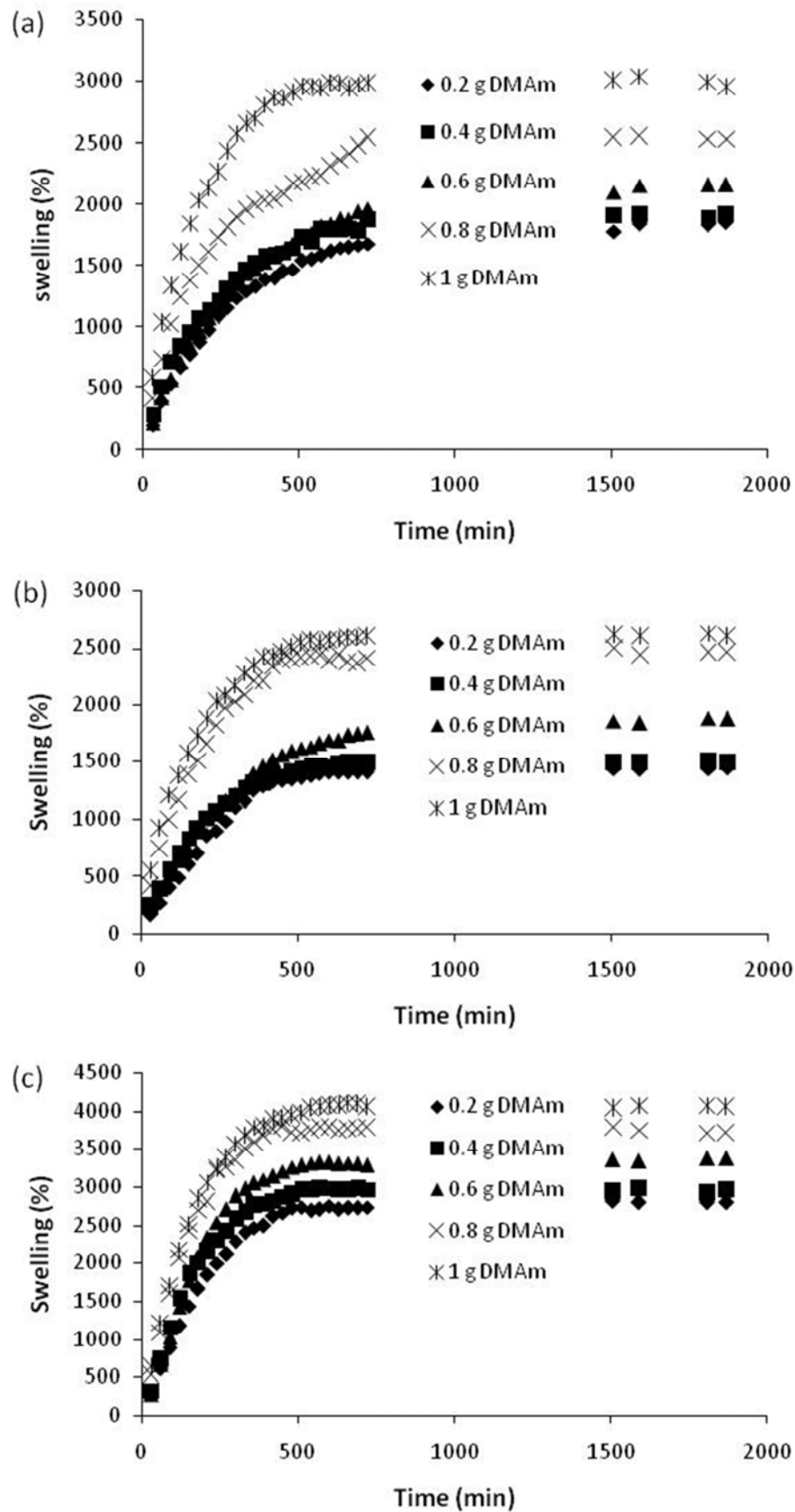
Figure 4. *Swelling curves of AA/AAm/DMAm hydrogels in (a) distilled water (b) buffer of pH=4 (c) buffer of pH=8.*

Table 2. *Swelling values of AA/AAm/DMAm hydrogels.*

Sample	Equilibrium swelling (%S_{eq})			Equilibrium water content (EWC)		
	DW	pH=4	pH=8	DW	pH=4	pH=8
P1	1757	1424	2769	0.9461	0.9344	0.9651
P2	1874	1494	2959	0.9493	0.9373	0.9673
P3	2050	1814	3336	0.9535	0.9477	0.9709
P4	2510	2430	3750	0.9617	0.9605	0.9740
P5	2984	2607	4068	0.9676	0.9631	0.9760

The results in Table 2 also show the effect of pH of buffer solution on the equilibrium swelling (S_{eq}) of hydrogel samples. Values of S_{eq} of AA/AAm/DMAm hydrogels in buffer solution of pH 8.0 is found to be significantly more in comparison to their equilibrium swelling in buffer solution of pH 4.0 and distilled water. It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. Under acidic pHs (≤4), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. Besides, there exist H-bonding interactions between carboxylic groups of acrylic acid and amide groups of acrylamide. These H-bonding interactions result in the formation of a compact or tight structure which does not permit much movement of polymeric chains within the hydrogel network, which lead to minimum swelling of hydrogel. As the pH of the swelling medium increased, the ionization of the carboxylic acid groups of the gel occurred. That resulted in a more hydrophilic

polymer network and contributed to the higher water absorption as the pH increased.

3.3. Equilibrium Water Content

Values of the equilibrium water content (EWC) of all the prepared hydrogel samples were estimated using equation (3) and were tabulated in Table 2. The data in Table 2 showed that values of the EWC of AA/AAm/DMAm hydrogels range from 0.9461-0.9676 in distilled water, 0.9344-0.9631 at pH 4 and 0.9651-0.9760 at pH 8. Generally, it is seen that an increasing by the adding of DMAm. Here, the main effect is the hydrophilic character of DMAm groups.

3.4. Swelling Kinetics

Once the hydrogel is immersed in a penetrating liquid, the penetrant diffuses into the hydrogel network and the hydrogel swells. The solvent migrates into pre-existing voids or dynamically formed spaces between hydrogel chains. Swelling of the hydrogels involves larger segmental motion resulting, ultimately, in increased separation between hydrogels chains. Based on experimental results, Schott [44, 45] has proposed the following model to describe polymer swelling:

$$t\,/\,S = A + Bt$$

Where S is the water uptake at time t, $B = 1/S_{eq}$ is the inverse of maximum or equilibrium swelling, $A = 1/k_s S_{eq}^2$ is the reciprocal of the initial swelling rate of the hydrogel material and k_s is the swelling rate constant. The final form of equation will be as follows.

$$t/s = 1/k_s S_{eq}^2 + 1/S_{eq}\, t \qquad (10)$$

Table 3. *Swelling kinetics parameters of AA/AAm/DMAm hydrogels.*

Sample	[a]S_{eq}			[b]$K_s \times 10^{-6}$			[c]K_{is}		
	DW	pH=4	pH=8	DW	pH=4	pH=8	DW	pH=4	pH=8
P1	2096	1628	3087	2.17	3.67	2.50	9.54	9.74	23.83
P2	2109	1622	3173	3.17	5.78	3.60	14.08	15.21	36.24
P3	2517	2146	3725	1.52	2.17	2.08	9.61	9.99	28.85
P4	2767	2649	3949	2.62	3.89	3.84	20.09	27.3	59.85
P5	3175	2776	4317	4.14	4.51	3.03	41.75	34.78	56.45

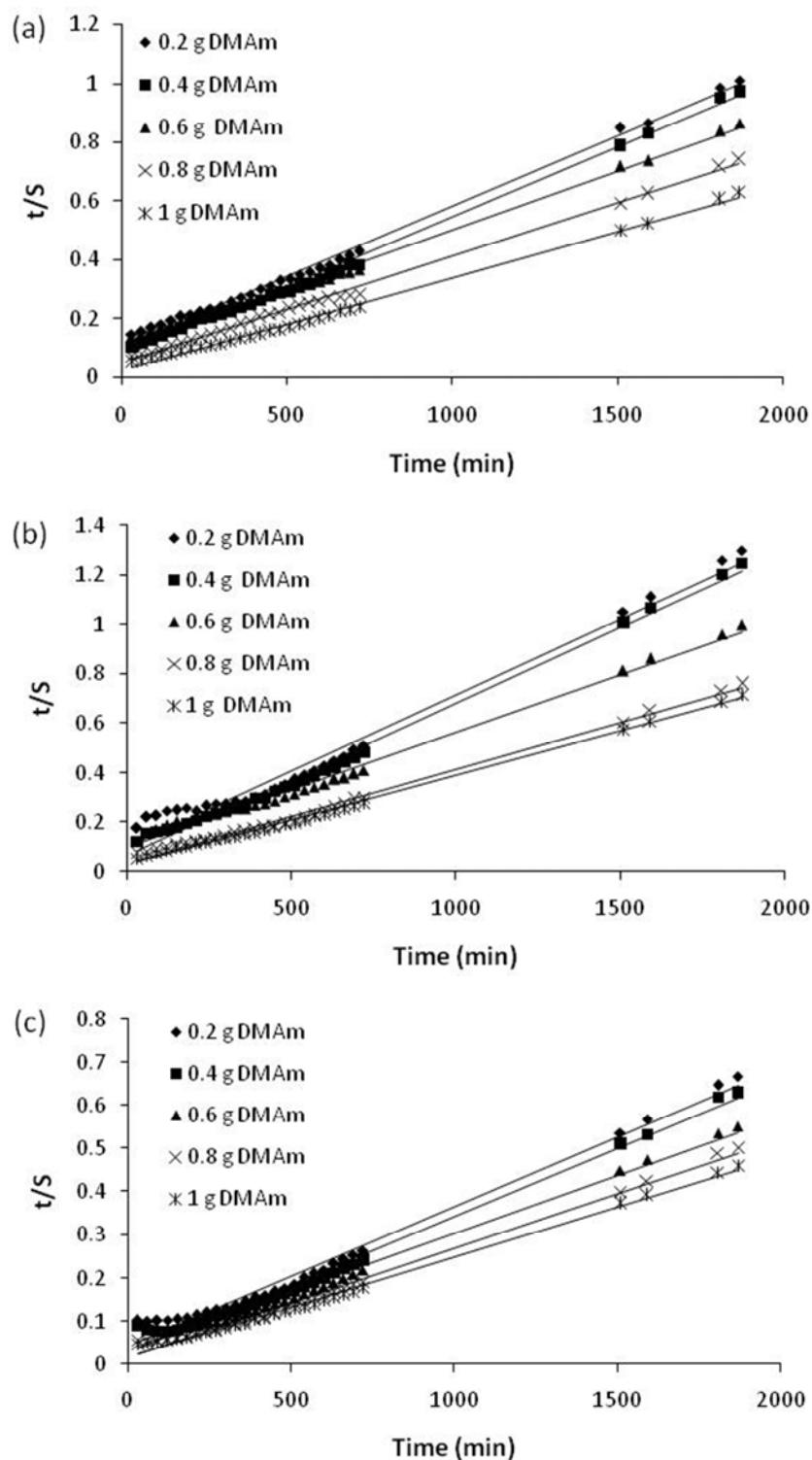[a] Theoretical equilibrium swelling; g$_{water}$/g$_{gel}$.
[b] Swelling rate constant (g$_{gel}$ /g$_{water}$)/min.
[c] Initial swelling rate, r (dS/dt)$_0$; (g$_{water}$/g$_{gel}$)/min.

The swelling kinetics curves are shown in Figure 5(a-c) by means of Eq. (10), where *t/S* is plotted against time t to give a straight line with good correlation coefficients for swelling results. From the slope and intercept of lines of Figure 5(a-c), values of swelling rate constant (k_s), the theoretical equilibrium swelling (S_{eq}) and the initial swelling rate (k_{is}) were calculated and the results are given in Table 3.

As shown in Table 3, the values of theoretical swelling

equilibrium S_{eq} are similar to the swelling results *%S_{eq}* presented in Table 2. Thus it can be concluded from these results that the swelling process is greatly affected by the chemical structure of the monomer repeat units in the polymeric network. Again, the initial swelling rate of AA/AAm/DMAm hydrogel systems is changed with DMAm content. This may be plausible since the hydrophilicity of the network is enhanced with the extent of DMAm groups in structure.

Figure 5. *Swelling kinetic curves of AA/AAm/DMAm hydrogel systems as a function of DMAm concentration in (a) distilled water, (b) buffer of pH=4 and (c) buffer of pH=8 at APE=50 mg.*

3.5. Scanning Electron Microscope

SEM micrographs of AA/AAm/DMAm hydrogel are presented in Figure 6. The SEM studies of hydrogels in presence of water is difficult, therefore the studies were carried out on dried hydrogels. The hydrogel samples were prepared without destroying their microstructure. The SEM photographs indicate that the prepared hydrogels have three dimensional porous structures. Existence of these pores and spongy surface in hydrogels strongly increases the swelling kinetics of the resulted product. It is supposed that these pores are the regions of the water permeation and interaction sites of water molecules with hydrophilic groups of hydrogel.
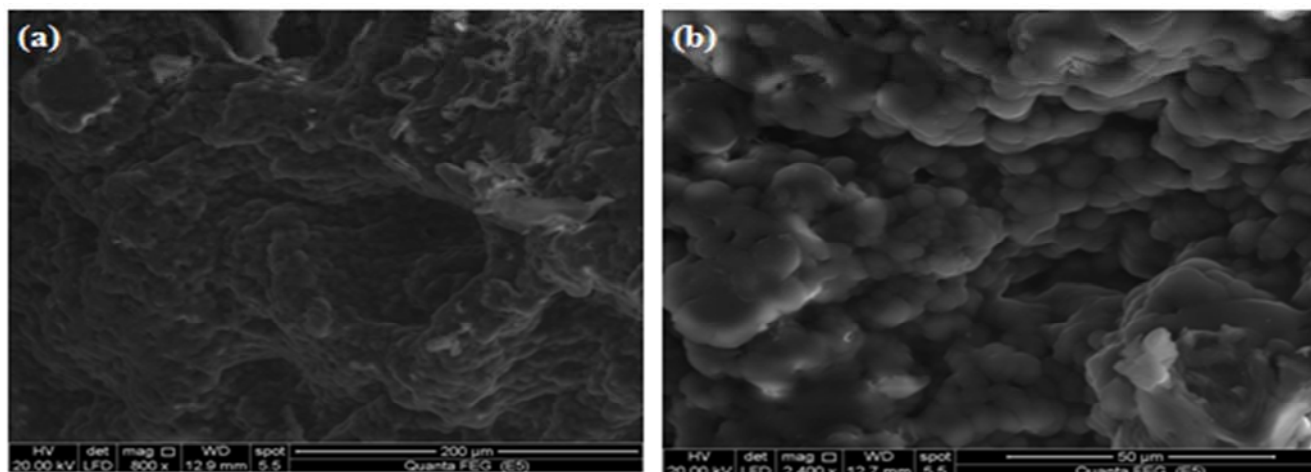
Figure 6. SEM photographs of AA/AAm/DMAm hydrogel at two different magnifications: a ×800, b ×2400.

3.6. Thermal Analysis

Representative TG thermograms of AA/AAm/DMAm hydrogel systems along with derivative thermograms (DTG) curve are shown in Figure 7a and TGA thermograms of all the prepared hydrogel samples are shown in Figure 7b. The TGA data are given in Table 4 which include the weight loss for all the prepared hydrogels at different temperatures such as T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{50} (temperature for 50% weight loss) and T_{max} (temperature for maximum weight loss). It is clearly seen from the figures that weight of the sample continuously decreases as the temperature increases.

TG curves of all the prepared hydrogel samples shows two stages of thermal degradation. The first stage of thermal degradation occurs upto 300°C and a weight loss of 22.9-23.7 % was observed. The weight loss in the first stage of thermal degradation may be due to water desorption and anhydride formation [46]. The second stage of thermal degradation is the major stage of degradation which occurs at 300-450°C and a weight loss of 63.7-65.1 % for AA/AAm/DMAm hydrogel systems was observed. This may due to the successive cleaving of the backbone of the polymeric hydrogels [46]. The weight loss was nearly constant when temperatures were higher than 450°C.

Table 4. TGA data of the prepared hydrogels.

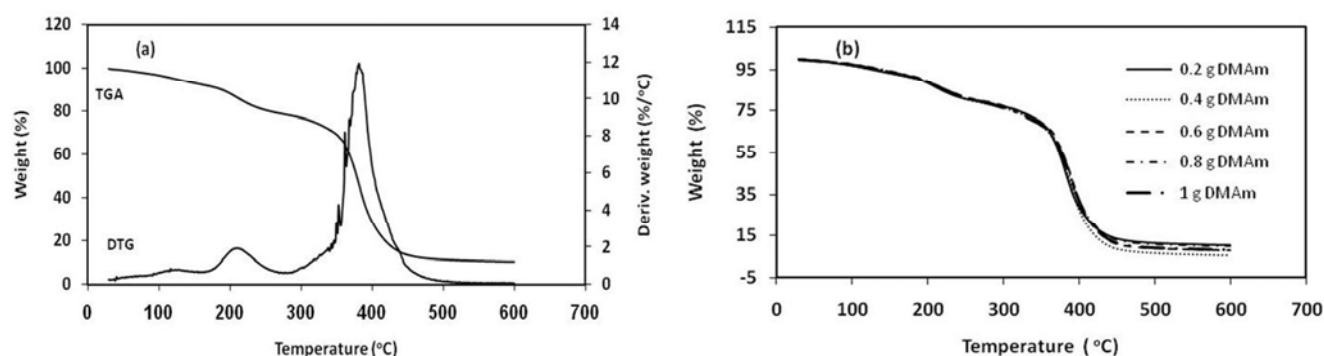| Sample	% Weight loss at various temperature(°C)					% wt. loss 300-450 (°C)	T_{10}(°C)	T_{20}(°C)	T_{50}(°C)	T_{Max}(°C)	
	200	300	400	500	600					StageI	StageII
P1	11.6	22.9	71.1	88.8	89.9	63.7	189	257	379	207	382
P2	11.4	23.6	72.3	93.4	94.5	67.7	192	255	380	205	390
P3	10.9	22.7	67.9	91.4	92.3	66.5	194	267	384	209	392
P4	10.8	22.9	68.3	89.3	90.3	64.3	195	265	382	212	387
P5	11.0	23.7	68.5	90.9	91.9	65.1	193	263	382	210	389

Figure 7. (a) Representative TGA and DTG of AA/AAm/DMAm hydrogel in inert atmosphere and (b)TGA curves of AA/AAm/DMAm hydrogels in inert atmosphere.

3.7. Dye Adsorption Studies of the Prepared Hydrogels

Out of the prepared hydrogel samples, P5 sample, which shows higher swelling capacity, was chosen for the adsorption of methylene blue cationic dye from aqueous solutions.

3.7.1. Effect of Contact Time

The effect of contact time on the adsorption of MB onto the prepared hydrogel at an initial concentration of 100 ppm from 0 to 720 min was investigated to identify the rate of dye removal. As depicted in Figure 8 the adsorption increases with the increasing contact time and rapid adsorption of MB was observed during the initial 200 min. The amount of MB adsorbed increased rapidly in the early stage and then increased more slowly over extended periods, gradually approaching adsorption equilibrium. This is due to availability of active binding sites on the sorbent at the initial stage. With gradual occupancy of binding sites, the sorption became slower in the later stage [47]. A contact time of 8 h was sufficient to reach equilibrium. Therefore sorption experiments were conducted for 8 hours.
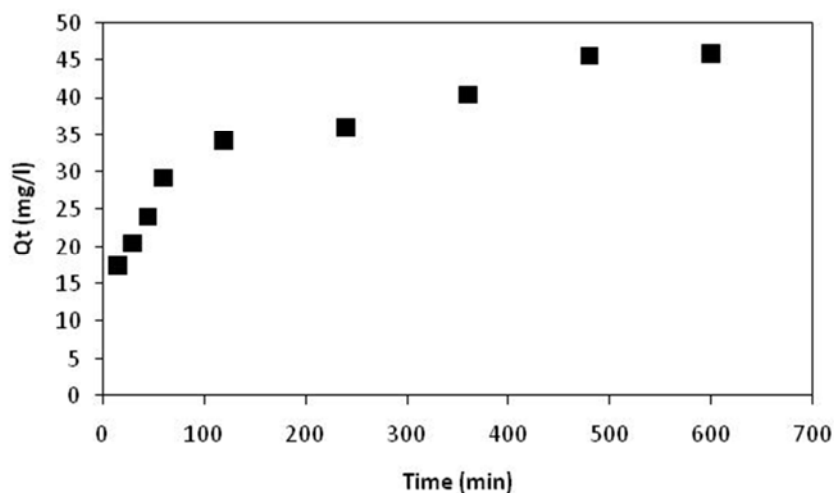

Figure 8. Effect of contact time on dye adsorption [C_o=100 mg/L and V=10 mL].
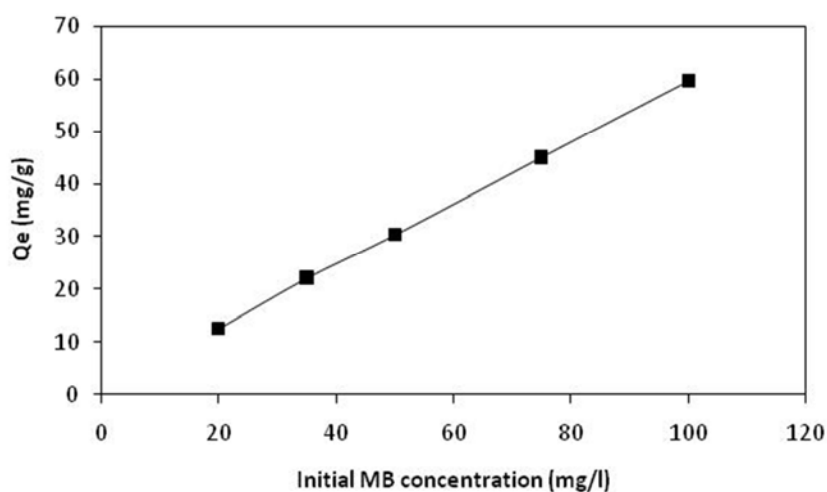

Figure 9. Effect of initial dye concentration (MB concentrations=20-100 mg/L, V=10 mL and t_{eq}=480 min).

3.7.2. Effect of Initial Dye Concentration

The effect of initial MB concentrations on adsorption by the prepared hydrogels is depicted in Figure 9. It is evident from the figure that the amount of dye adsorbed Q_e increased when the initial concentration was increased from 20 to 100 mg L^{-1}. These results suggest that the initial dye concentration is an important factor that determines the efficiency of the adsorption process. The lowest amount of dye adsorbed at lower initial dye concentration may be explained by unsaturated adsorption due to the presence of remaining free adsorption sites.

3.7.3. Effect of pH

The initial pH of the dye solution is an important factor that determines the adsorption behavior. This dependence is due to variation of the surface properties with the pH. These properties include surface charge, chemistry, and number of active sites. The dye adsorption by hydrogels may be explicated by adsorption transport mechanism into swollen polymer networks. The higher water content and porous structure networks allow for solute diffusion through the hydrogel structure. When a hydrogel is dipped in an aqueous medium, it begins to absorb water, resulting in considerably changes of its polymer structure. The dye molecules, upon contact with water, may or may not penetrate into hydrogel depending on established interactions between dye molecules and polymer chains. Effect of pH on adsorption was studied using 100 mg L^{-1} dye concentration, pH 3,4,7 and 8 at 25°C.

The results shown in Figure 10 indicate that the lowest dye adsorption was recorded at pH 3. The equilibrium adsorption (Q_e) was found to increase with increasing pH. Lower adsorption of MB at acidic pH is probably due to the presence of excess H$^+$ ions competing with the cation groups on the dye for adsorptionsites. At higher pH, the surface of the hydrogel particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction [48, 49]. This can be explained as follow: At higher pH, the carboxylic groups COOH present in the hydrogel dissociate to form COO−, increasing the number of fixed ionized groups. This generates electrostatic repulsion forces among the adjacent ionized groups of polymer networks, inducing an expansion of the polymer chains within the hydrogel structure. In this logic, the formation of an ionic complex between the MB molecules and the hydrogel networks is provided, increasing the dye removal. These interactions occur more precisely between the dye imines groups and the charged groups of the polymer networks.
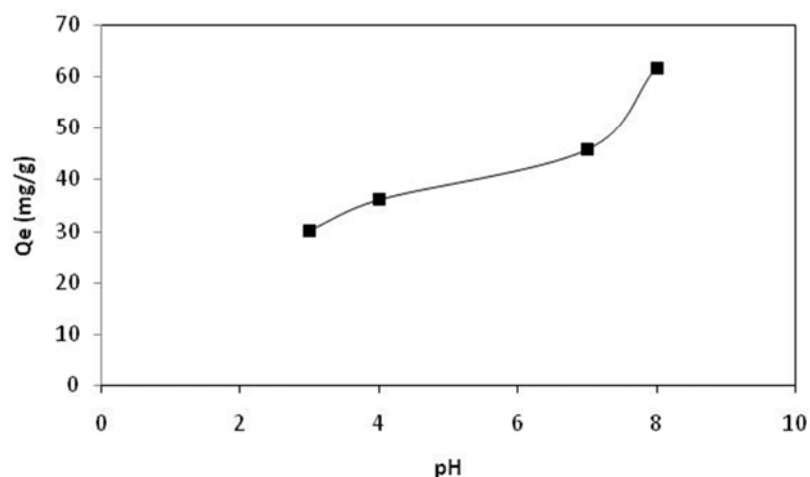

Figure 10. Effect of pH on MB removal (MB concentration=100 mg/L, volume of sample=10 mL and equilibrium time=480 min).

3.7.4. Sorption Kinetics

In this study, the pseudo-first-order equation and pseudo-second-order equation were used to describe the adsorption of MB on the prepared hydrogels. The pseudo-first-order kinetic model was suggested by Lagergren [50] for the adsorption of solid/ liquid systems. Values of $\ln(Q_e - Q_t)$ and t/Q_t were calculated using the equations described in the experimental section. Linear plots of $\ln(Q_e - Q_t)$ and t/Q_t against t were constructed and used for calculating the kinetic parameters (Figure 11). The calculated kinetic parameters are shown in Table 5. It can be seen from Figure 11 that the Pseudo-second-order kinetic model gave the best fitting of the kinetic data. Using the calculated kinetic models parameters (Table 5), the equilibrium adsorption amount predicted by Pseudo-second-order kinetic model ($Q_{e,calc}$) is very close to the measured value ($Q_{e,exp}$), and the correlation coefficient R^2 is more than 0.995. These results suggest that the pseudo-second-order kinetic model closely describes the sorption process of MB on the prepared hydrogel. It implies the adsorption process is probably a chemical process [51]. And the chemisorption could be rate limiting in the sorption step involving ion exchange of sorbent and sorbate [37]. The correlation coefficients (R^2) for the pseudo first- order kinetic model are lowest in comparison to the values obtained for the pseudo-second-order kinetic model. Moreover, a large difference between $Q_{e,calc}$ and $Q_{e,exp}$ was observed, indicating a poor pseudo-first-order fit to the experimental data.
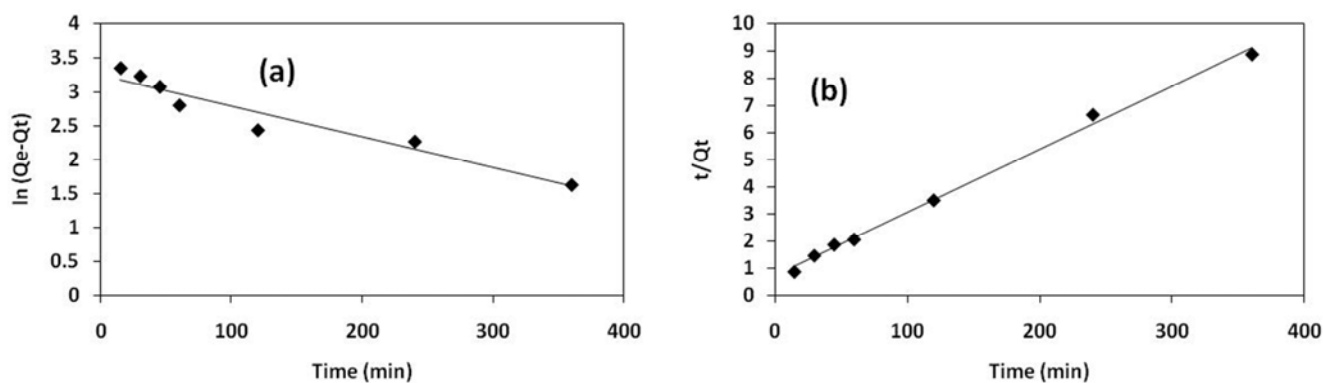

Figure 11. *Adsorption kinetics of MB onto AA/AAm/DMAm according to (a) Pseudo first order model (b) Pseudo second order model[C_o=100 mg/L, pH=7 and T=25ºC].*

Table 5. *Adsorption kinetic parameters for MB adsorption on the hydrogels.*

Sample	Pseudo-First-Order			Pseudo-Second-Order			Exp.
	$k_1(min^{-1})$	$Q_e(mg/g)$	R^2	$k_2(g\ mg^{-1}\ min^{-1})$	$Q_e(mg/g)$	R^2	$Q_e(mg/g)$
AA/AAm/DMAm	4.55×10^{-3}	25.68	0.930	5.1×10^{-4}	47.07	0.995	45.7

3.7.5. Adsorption Isotherms

The adsorption isotherms are important for description how the molecules of adsorbate distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The experimental data on the effect of initial MB concentrations on adsorption by the prepared hydrogels (see Figure 12) were fitted to Langmuir and Freundlich models, which were obtained by plotting C_e/Qe versus C_e and log Q_e versus log C_e, respectively. All isotherm model parameters are presented in Table 6.
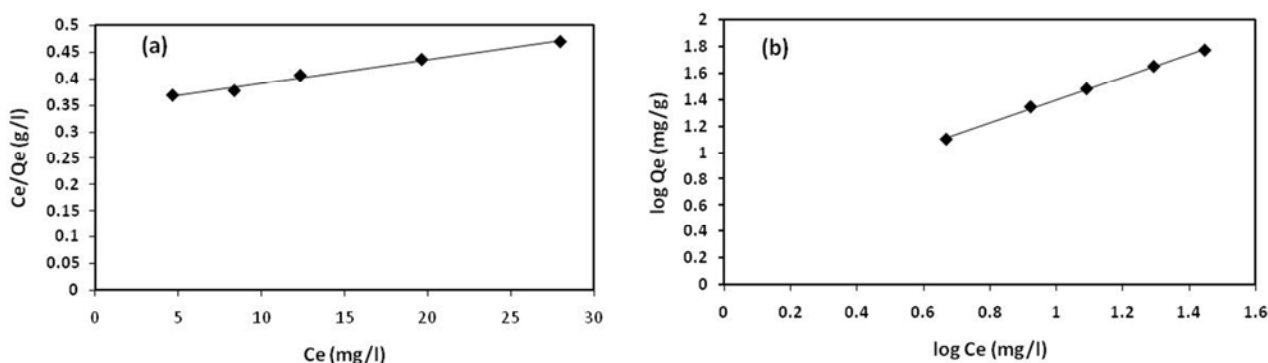
It can be seen that the correlation coefficient (R^2) of Freundlich isotherms is 0.998; however, R^2 values of the Langmuir isotherms are less than those of Freundlich isotherms. These differences in correlation coefficients indicate that the adsorption of MB on the prepared hydrogel followed the Freundlich model more closely than it followed the Langmuir model. This result suggests that binding of MB occurs on the heterogeneous surface of the hydrogel by multilayer adsorption process.

Figure 12. *Adsorption isotherms of MB onto AA/AAm/DMAm according to (a) Langmuir model (b) Freundlich model[C_o=100 mg/L, pH=7 and T=25°C].*

Table 6. *Adsorption isotherm parameters for MB adsorption on the hydrogels.*

Sample	Langmuir model			Freundlich model		
	K_L	$Q_m(mg/g)$	R^2	K_f	n	R^2
AA/AAm/DMAm	0.012936	223.2031	0.989	3.45295517	1.16176352	0.998

4. Conclusion

In this study, AA/AAm/DMAm hydrogels were prepared by free radical polymerization in solution. Hydrogels were swollen to equilibrium in water. It was found that the adsorption capacity of the prepared hydrogels increases by increasing the DMAm content. Hydrogel systems swelled in the range 1757-2984 % in distilled water, 1424-2607 % at pH 4 and 2769-4068 % at pH 8. The values of EWCs were found to be in the range 0.9461-0.9676 in distilled water, 0.9344-0.9631 at pH 4 and 0.9651-0.9760 at pH 8. This result showed that AA/AAm/DMAm hydrogels would be used as a new material (such as a biomaterial) on some biomedical applications, because EWCs was bigger than the percent water content value of the body about 0.60. The hydrogel was also used in adsorption of the MB dye from aqueous solutions. It was found that the adsorption kinetics of hydrogels followed a pseudo-second-order model. Equilibrium isotherms were analyzed using the Langmuir and Freundlich isotherms. It was seen that the Freundlich model fits the adsorption data better than the Langmuir model. Therefore, AA/AAm/DMAm can be used as effective adsorbents for the removalof MB from wastewaters.

Acknowledgement

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